MASTER

ARF 2198-15
(Quarterly Report)
EURAEC- 87

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

IMPROVED ZIRCONIUM ALLOYS

U.S./EURATOM PROGRAM
Contract No. AT(11-1)-578
Project Agreement No. 1

25 years of research

ARMOUR RESEARCH FOUNDATION
of
ILLINOIS INSTITUTE OF TECHNOLOGY
Technology Center
Chicago 16, Illinois

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January 1, 1961 - March 31, 1961
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U.S./EURATOM PROGRAM
Joint Research and Development Board
51-53 rue Belliard
Brussels, Belgium

April 11, 1961

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I. SUMMARY OF PROGRESS TO DATE

The development of improved zirconium alloys for service in superheated water and steam has involved the preparation of some 100 compositions by arc melting followed by hot rolling. Initial studies are being concentrated on twenty-five binary systems and seven zirconium-niobium base ternary systems. A complete list of the alloys under investigation was presented in the previous Quarterly Report (ARF 2198-11).

Corrosion testing of these alloys has been conducted in 680°F water for times up to 1903 hours; control specimens of Zircaloy-2 were included in these tests. Some fifty compositions which exhibited promising corrosion behavior in 680°F water are being tested in 750°F steam. At the end of the current reporting interval, 455 hours of exposure time had been accumulated on these specimens. Corrosion tests of some of the more promising alloys have also been conducted in 900°F steam. Data are available for the initial exposure period of 97 hours. Results of these tests in superheated water and steam form the basis for the planning of ternary and more complex zirconium-base compositions.

The effect of zirconium purity on corrosion behavior is under study. Specimens of iodide and sponge zirconium have been refined by electron-beam melting. Hardness and metallographic studies have been conducted on these materials, and sheet samples have been prepared for corrosion testing.

Preliminary transformation kinetics studies have been conducted in beta-quenched specimens of Zr-30Nb and Zr-30Nb-5Mo* alloy to evaluate the stability of retained beta at 680°F. Hardness measurements have been taken after annealing times of 350 hours. Sheet samples of the ternary alloy in the retained beta condition have been prepared for evaluation of corrosion behavior.

* Compositions are reported in weight per cent.

Tensile test data have been obtained for ten of the zirconium-base alloys under investigation. The test temperature was 680° F, and a sample of Zircaloy-2 was included for purposes of comparison.

II. PRINCIPAL INVESTIGATORS

D. Weinstein	-	Project Engineer
F. C. Holtz	-	Group Leader

III. STATEMENT OF PROBLEM

This program has as its objective the development of zirconium-base alloys having superior 680° F water and/or 750° to 900° F steam corrosion resistance. The development of alloys having higher strength than Zircaloy-2 at current temperature ranges is also a major program objective. These studies include an evaluation of the effect of heat treatment on corrosion resistance; retained beta structures in Zr-Nb base alloys will be corrosion tested. In addition, the effects of zirconium purity on corrosion resistance, and hydrogen pickup during corrosion will be determined for promising compositions.

IV. DESCRIPTION OF WORK--RESULTS

Major efforts under the current program have been devoted to an evaluation of corrosion resistance of a wide range of binary zirconium-base alloys; several ternary zirconium-niobium base materials were also studied. Corrosion behavior will be used in planning of ternary and higher order alloys. Table I presents the results of corrosion tests in 680° F water, and in 750° and 900° F steam for alloys in the alpha-annealed condition. Materials having unacceptable corrosion resistance (high weight gain or white oxide coating) are designated by an asterisk; the remaining compositions are being tested for additional periods of time. Alloy systems of interest in 680° F water include Zr-(Nb, Sb, Cr).

Test results after 329 hours in 750° F steam show corrosion minimums in the Zr-V and Zr-Sb systems, and increasing tin levels produce improved corrosion resistance. Certain compositions in the systems Zr-(Nb, Fe, Mo, Pd) also exhibit promising preliminary corrosion properties in 750° F steam. Initial test data in steam at 900° F showed promising behavior for Zr-0.5Nb, Zr-1V, Zr-3Cr alloys, and for the Zr-Fe and Zr-Mo systems. Of particular interest would be the 900°F steam corrosion resistance of binary alloys containing greater than 3 per cent iron. These data, being of a preliminary nature are used for determining the effect of alloy additions on corrosion resistance; they do not necessarily indicate acceptability of any particular binary alloy as a fuel cladding.

Tensile data at 680°F were obtained on selected compositions for the purpose of determining the relative strengthening effect of alloy additions. As indicated in Table II, Zr-1V exhibits relatively high strength and moderate ductility. Thus, the tensile properties and steam corrosion behavior indicate that Zr-1V is a highly promising alloy and would warrant further development effort. The compositions Zr-1Sb and Zr-1Mo may be similarly classified.

V. FUTURE WORK

At the end of the current reporting period, corrosion testing of promising compositions was being continued in 680°F water, and in 750° and 900°F steam. The present contract is scheduled to be terminated on April 30, 1961; corrosion data will be accumulated to that date. In anticipation of a possible continuation of this work, a number of ternary alloys are being planned. Longer-time corrosion data, especially in steam at 750° and 900°F, will be required for evaluation of binary systems, so that more complex alloys can be prepared for higher temperature service. Other corrosion studies will include the testing of alloys prepared from electron-beam melted zirconium stock, and also the evaluation of corrosion resistance of retained beta alloys including Zr-30Nb-5Mo.

As ternary or higher order alloys having promising corrosion resistance are developed, these materials will be evaluated for tensile strength and other mechanical properties in the temperature range of 680° to 900°F. In addition, studies of hydrogen pickup during corrosion will also be conducted on the more promising compositions.

VI. CONCLUSION

This program is concerned with the development of zirconium-base alloys having improved corrosion resistance and/or strength. A major improvement over Zircaloy is desired, and the approach to this development involves screening (by corrosion resistance) a wide range of binary alloys. As originally planned, these data would manifest promising compositions and therefore allow logical planning of ternary and higher order alloys. Indeed, the binary screening program has indicated a number of promising compositions for both water and steam service, and ternary alloys are being planned.

VII. REPORTS ISSUED

D. Weinstein, F. C. Holtz, and R. J. Van Thyne, "Improved Zirconium Alloys", Summary Report, ARF 2198-13, U.S./EURATOM PROGRAM, February 28, 1961.

Respectfully submitted,

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

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TABLE I

CORROSION BEHAVIOR OF BINARY ZIRCONIUM ALLOYS IN SUPERHEATED WATER AND STEAM

Composition	680° F Water 1043 hr	680° F Water 1902 hr	750° F Steam 329 hr	900° F Steam 97 hr
Zircaloy-2	26.83	30.33	24.88	a*
Zr-0.5Nb	27.57	34.18	27.42	65.05
Zr-2Nb	47.44	44.80* a	51.20	111.40*
Zr-5Nb	removed after 355 hr		72.20*	126.68*
Zr-10Nb	removed after 355 hr		101.75*	----
Zr-25Nb	126.04*	----	136.46*	----
Zr-30Nb	98.86	131.47	134.73	264.40*
Zr-0.5Sn	20.58	21.61	a*	----
Zr-1.5Sn	28.68	123.93	1202.88* a	----
Zr-3Sn	31.91	293.38*	4763.23*	----
Zr-5Sn	26.52	113.22	603.63*	----
Zr-7Sn	61.90*	----	252.18	a*
Zr-10Sn	removed after 168 hr		in test	a*
Zr-12Sn	removed after 168 hr		in test	a*
Zr-0.25V	29.49	40.67*	277.41* a	a*
Zr-1V	38.58	57.86*	27.19	69.05
Zr-3V	removed after 168 hr		a*	a*
Zr-5V	removed after 168 hr		----	647 a*
Zr-9V	removed after 168 hr		----	a*
Zr-0.25Sb	335.64*	----	1745.0 a*	a*
Zr-1Sb	30.64	33.81	29.51	a*
Zr-2.5Sb	37.68	51.28*	37.01	a*
Zr-4Sb	53.77*	----	41.65	527.61*

TABLE I (continued)

Composition	680° F Water 1043 hr	680° F Water 1902 hr	750° Steam 329 hr	900° F Steam 97 hr
Zr-6Sb	removed after 355 hr		75.40	773.10*
Zr-0.25Cr	19.57	19.57	22.44	a*
Zr-1Cr	23.38	27.45	58.44	a*
Zr-3Cr	67.82*	----	23.09	51.87
Zr-0.25Cu	30.76	32.95	24.78	a*
Zr-0.25Fe	22.42	26.50	26.77	119.64 a*
Zr-1Fe	36.82	45.00*	27.79	86.10*
Zr-3Fe	40.42*	----	38.65	77.13
Zr-0.25Si	33.39	37.44*	56.96* a	-----
Zr-0.25W	14.34	17.95	671.19 a*	-----
Zr-1W	256.82*	----	652. a*	-----
Zr-0.25Mo	22.26	23.28	17.04	54.29
Zr-1Mo	52.33*	----	20.08	58.78
Zr-3Mo	removed after 168 hr		----	246.31*
Zr-0.25Ta	21.86	28.81	35.31	-----
Zr-0.25Co	31.35	33.51	38.90	82.21 a*
Zr-1Co	27.55	28.93	27.30	85.73
Zr-3Co	38.47	47.83	33.13	129.96*
Zr.0.25Pt	28.27	89.16*	37.84	-----
Zr-1Pt	46.67	45.58 a*	54.43*	-----
Zr-0.25Pd	44.06	50.51	34.53	95.50*
Zr-1Pd	49.98	69.39*	48.83	70.87
Zr-3Pd	removed after 168 hr		----	147.18*
Zr-0.25Rh	36.65	39.27	40.31*	-----
Zr-1Rh	26.40	54.12*	53.91*	-----

TABLE I (continued)

Composition	680°F Water 1043 hr	680°F Water 1902 hr	750°F Steam 329 hr	900°F Steam 97 hr
Zr-0.25As	21.87	26.24	131.27*	-----
Zr-1As	16.40	35.54	a*	-----
Zr-0.25Bi	removed after 355 hr		1481.27 a*	-----
Zr-0.25Te	24.12	27.40	19.01	-----
Zr-1Te	47.88	62.03*	39.09	-----
Zr-0.25Ge	35.73	38.38*	43.30*	-----
Zr-1Ge	removed after 355 hr		202.96 a*	-----
Zr-1Ag	33.73	41.35	1916.99 a*	-----
Zr-0.25Ni	34.52	37.75	32.84	a*
Zr-1Ni	41.14	48.72	33.23	123.58*
Zr-3Ni	removed after 355 hr		103.25*	141.92

* Unacceptable corrosion resistance--discontinued from further testing.

a Oxide coating lifting from metal subsurface or severe spalling and disintegration occurred.

-- No test.

TABLE II

TENSILE PROPERTIES OF SELECTED EXPERIMENTAL ALLOYS AT 680°F

Composition	Ultimate Tensile Strength (psi)	Elongation (1 in.) (per cent)
Unalloyed Zr	16,000 *	45 *
Zircaloy-2	29,400	33
Zr-0.5Nb	23,800	16
Zr-1.5Sn	27,500	20
Zr-10Sn	80,600	5
Zr-1Fe	25,600	19
Zr-1V	40,000	17
Zr-1Cr	22,000	14
Zr-1Mo	32,800	12
Zr-1Sb	29,000	17
Zr-1Co	22,000	26

* Obtained from literature.